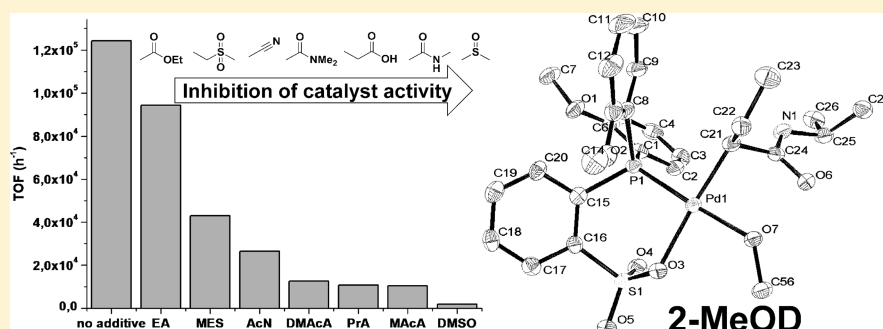


Mechanistic Insights into Polar Monomer Insertion Polymerization from Acrylamides

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Supporting Information



ABSTRACT: *N*-Isopropyl acrylamide (NIPAM), *N,N*-dimethyl acrylamide (DMAA), and 2-acetamidoethyl acrylate (AcAMEA) were copolymerized with ethylene employing [(P[^]O)PdMe(DMSO)] (**1**-DMSO; P[^]O = κ^2 -P,O-Ar₂PC₆H₄SO₂O with Ar = 2-MeOC₆H₄) as a catalyst precursor. Inhibition studies with nonpolymerizable polar additives show that reversible κ -O-coordination of free amide retards polymerization significantly. Retardation of polymerization increases in the order ethyl acetate $\ll$ methyl ethyl sulfone < acetonitrile < *N,N*-dimethylacetamide $\approx$ *N*-methylacetamide $\approx$ propionic acid < dimethylsulfoxide. Pseudo-first-order rate constants for the insertion into **1**-DMSO were determined to increase in the order DMAA < AcAMEA < NIPAM < methyl acrylate. Exposure of **1**-DMSO to NIPAM resulted in the formation of consecutive insertion products [(P[^]O)Pd(C₆H₁₁NO₂)_{*n*}Me] (*n* $\leq$ 3), as determined by electrospray ionization mass spectrometry. The solid-state structure of the methanol adduct of the 2,1-insertion product of NIPAM into **1**-DMSO, [(P[^]O)Pd{ η^1 -CH(CONHiPr)CH₂CH₃}(κ^1 -O-MeOD)] (**2**-MeOD), was determined by single crystal X-ray diffraction. Both 2,1- and 1,2-insertions of DMAA into the Pd–Me bond of a [(P[^]O)PdMe] fragment occur to afford a ca. 4:1 mixture of chelates [(P[^]O)Pd{ κ^2 -C,O–C(CH₂CH₃)C(O)NMe₂}] (**3**) and [(P[^]O)Pd{ κ^2 -C,O–CH₂C(CH₃)C(O)NMe₂}] (**4**). The four-membered chelate of **3** is opened by coordination of 2,6-lutidine (**3** + 2,6-lutidine $\rightleftharpoons$ **3**-LUT) with $\Delta H^\circ = -41.8(10.5)$ kJ and $\Delta S^\circ = -115(37)$ J mol⁻¹ K⁻¹.

INTRODUCTION

Catalytic insertion polymerization of ethylene and propylene is one of the most well-studied chemical reactions. In terms of applications, it is employed for the production of more than 70 million tons of polyolefins annually.¹ An insertion (co)-polymerization of electron-deficient polar-substituted vinyl monomers like acrylates has remained a challenge, however.

Considerable progress in this area has been achieved by the development of d⁸-metal (late transition metal) complexes. Their less oxophilic nature, in comparison with their early transition metal counterparts, renders them more tolerant toward polar moieties.² In the mid 1990s, cationic Pd(II) α -diimine complexes were reported to catalyze the insertion copolymerization of ethylene and 1-olefins with acrylates. Because of the “chain walking” of the catalyst, the highly branched copolymers contain acrylate units preferentially at the end of branches. The mechanism of this branch formation is well understood from extensive variable temperature NMR studies.³ Such studies have also provided an understanding of the problems associated with monomers not amenable to

polymerization with these catalysts, like vinyl acetate or vinyl chloride. β -X elimination (X = acetate, chloride) is one significant decomposition route.^{4,22} In contrast, with neutral Pd(II) phosphinesulfonato complexes, linear copolymers of ethylene with a broad scope of polar vinyl monomers including acrylonitrile, vinyl acetate, and acrylic acid are formed.^{2h,5–7} These catalysts have been studied as in situ mixtures of Pd^{II} or Pd⁰ sources and ligands⁸ and employing [(P[^]O)PdMe(L)] (L = pyridine, 2,6-lutidine, PPh₃, 1/2 Me₂NCH₂CH₂NMe₂, dimethylsulfoxide) complexes as well-defined single-component catalyst precursors.⁹ Recent experimental and theoretical mechanistic studies on the key intermediates of the insertion (co)polymerization of acrylates, κ^2 -C,O-coordinated Pd(II)-alkyl species [(P[^]O)Pd{ κ^2 -CH(C(O)OMe)CH₂CH(C(O)OMe)CH₂CH₃}], resulting from two consecutive 2,1-insertions of MA, showed that the chelating κ -O-coordination of the

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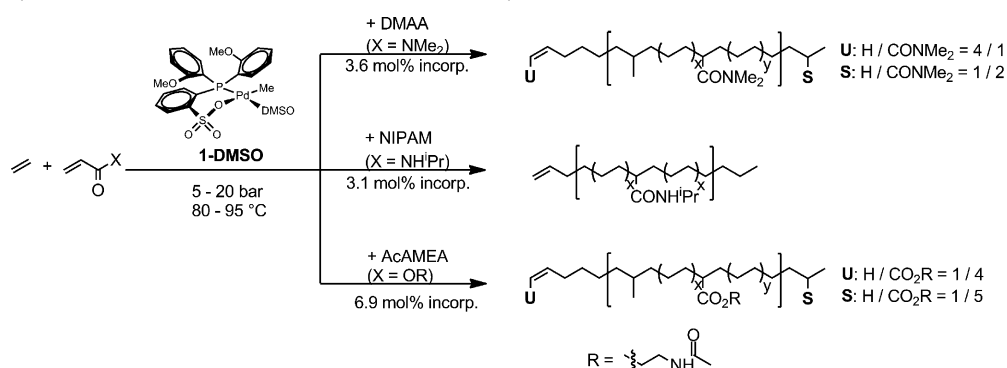


Table 1. Copolymerization with Ethylene^a

entry	comon.	T [°C]	p [bar]	comon. conc. [mol L ⁻¹]	polymer yield [g]	TOF ^b C ₂ H ₄	TOF ^b comon.	X _{AA} ^{c,d}	M _n ^e [10 ³ g mol ⁻¹]	M _w /M _n ^e
1-1	NIPAM	80	20	0.2	0.365	619	3	1.7	5.8	2.0
1-2	NIPAM	80	20	0.5	0.110	183	1	2.4	3.4	2.0
1-3	NIPAM	80	20	1.0	0.044	72	1	3.1	2.4	1.7
1-4	DMAA	80	20	0.2	1.085	1922	3	0.6	9.6	2.0
1-5	DMAA	95	20	0.2	1.402	2482	5	0.7	6.8	2.1
1-6	DMAA	95	10	0.2	0.568	1000	3	1.2	4.3	2.2
1-7	DMAA	93	5	0.2	0.260	456	2	1.7	3.1	2.1
1-8	DMAA	90	5	1.0	0.051	88	1	3.6	1.2	1.5
1-9	DMAA	90	20	2.2	0.042	72	1	3.5	1.5	1.6
1-10 ^f	AcAMEA	95	5	0.2	0.160	266	4	6.9	0.7	1.4

^aReaction conditions: 20 μ mol **1-DMSO**; total volume toluene + comonomer, 50 mL; polymerization time, 1 h. ^bTOF in mol(monomer incorporated) mol(catalyst)⁻¹ h⁻¹. ^cMolar incorporation in copolymer. ^dFrom ¹H NMR in C₂D₂Cl₄ at 130 °C. ^eFrom GPC at 160 °C in 1,2,4-trichlorobenzene vs linear polyethylene. ^fMicro size reactor with 5 mL total reaction volume of the liquid phase.

Scheme 1. Copolymerization of Amide Comonomers with Ethylene (U = Unsaturated and S = Saturated Chain End)



second last inserted acrylate unit significantly retards further chain growth.^{10,11}

Materials containing amide moieties are of general interest due to the exceptional hydrogen-bonding ability of amides, which can be reflected in specific properties and structures. However, reports of amide-containing (co)polymers obtained by insertion polymerization are rare. The copolymerization of acrylamides passivated with aluminum alkyls by α -diimine Ni(II) complexes was reported to yield copolymers with low acrylamide contents (<5 mol %).¹² Clavier et al. communicated the preparation of linear ethylene-*N,N*-isopropylacrylamide (NIPAM) and ethylene-*N*-vinyl-2-pyrrolidone copolymers with Pd(II) phosphinesulfonate complexes [(P[^]O)PdMe(pyridine)] as catalyst precursors.^{6d,13} An exclusive in-chain incorporation of NIPAM was observed, and no NIPAM-derived chain ends were detected. Beyond these findings, no comprehensive picture of the properties of amides in insertion polymerizations and a mechanistic understanding exist. We now give a full account of the reactivity of acrylamides in insertion (co)polymerizations catalyzed by neutral phosphine-sulfonate Pd(II) complexes and rationalizations on polar monomer insertion polymerization in general from the insights gained.

RESULTS AND DISCUSSION

Copolymerization Studies and Copolymer Microstructure. The copolymerization of ethylene with the tertiary amide dimethylacrylamide (DMAA), and for comparison also with NIPAM, was studied (Table 1 and Scheme 1). As a catalyst precursor, the DMSO-coordinated complex [(P[^]O)-PdMe(DMSO)] (P[^]O = 2-[di(2-methoxyphenyl)phosphino]-

benzenesulfonate) (**1-DMSO**) was employed. Because of the relatively weak binding of DMSO by comparison to other stabilizing ligands, such as pyridine, polymerizations can be performed with reasonable activities also at low ethylene pressure and thus at high [comonomer]/[ethylene] ratios.^{9e} At a relatively high [DMAA]/[ethylene] ratio ([DMAA] = 1 mol L⁻¹ and p(ethylene) = 5 atm; entry 1-8), an incorporation of the tertiary amide of 3.6 mol % was observed. As expected, at a given ethylene pressure, the incorporation of amide in the polymer increases with the concentration of acrylamide monomer in the reaction mixture (entries 1-5 vs 1-9 and 1-7 vs 1-8). At the same time, productivity decreases significantly. Likewise, at a given acrylamide concentration, the ethylene content of the copolymers increases with ethylene concentration, and notably productivity also increases (entries 1-5 to 1-7). These findings already indicate that amide functions retard the polymerization reaction. The catalyst was stable over the time of the reaction and showed single site behavior as concluded from molecular weight distributions M_w/M_n around 2. A comparison of the copolymer compositions formed under identical reaction conditions, and of the reaction conditions under which copolymers of similar degree of incorporation of amide are formed, shows that DMAA competes less efficiently with ethylene incorporation than NIPAM.

By comparison to previous studies of ethylene-methyl acrylate (MA) copolymerization, the activities and incorporations in the copolymerizations of amides (cf. Table 1) are lower. Under otherwise similar conditions (5 atm ethylene, [MA] = 0.6 mol L⁻¹, 95 °C), **1-DMSO** yielded 2.57 g of an ethylene-MA copolymer with 9.4 mol % MA content.^{9e} To shed light on the origin of this different behavior,

copolymerizations of 2-acetamidoethyl acrylate (AcAMEA) (entry 1-10) were studied. Whereas the copolymer was obtained in a comparably low yield of 0.15 g, the incorporation rate of 6.9 mol % AcAMEA was about two times higher than in the ethylene–acrylamide copolymerizations. As expected, these incorporations are more similar to MA incorporation, and the lower incorporation of AcAMEA vs MA can be rationalized by the higher steric bulk of the former, which disfavors coordination vs the ethylene comonomer. The lower yield suggests that amide moieties in the monomer in general, also in a remote position, hinder the polymerization reaction (vide infra).

High-temperature NMR spectroscopy (see the Supporting Information) unambiguously confirmed the copolymer nature of the materials. The composition of the end groups was of particular interest as the reported ethylene–NIPAM and –NVP copolymers did not show end groups derived from polar monomer,^{6d} which differs from copolymers of ethylene and other electron-withdrawing substituted polar vinyl monomers obtained with Pd(II)–phosphinesulfonato complexes where usually the majority of end groups are based on the polar vinyl monomer. The ethylene–NIPAM copolymers obtained here with 1-DMSO (entries 1-1 to 1-3) possessed no observable NIPAM-derived end groups, in accordance with previous findings by Clavier et al.^{6d} In the ethylene–DMAA copolymer with 3.5 mol % incorporation (entry 1-9), DMAA-based repeat units were found to be incorporated in-chain, in saturated, and in unsaturated chain-ends in a ratio of 6:3:1. The ratio of saturated ethylene- and DMAA-derived end groups was found to be 1:2, which roughly reflects the concentration of the monomers¹⁴ in the reaction mixture; that is, there is no strong preference for one of the monomers regarding insertion into a Pd–H bond. This differs from chain growth by insertion into alkyls, in which ethylene is preferred over the polar monomer (Scheme 1). Accordingly, no saturated end groups resulting from an insertion of DMAA and AcAMEA into the Pd–Me bond of 1-DMSO were observed. In the unsaturated end groups, ethylene-derived groups prevail by ca. 4:1. Considering that the incorporation ratio of ethylene vs DMAA in the polymer backbone is ca. 30, this indicates that β -H elimination occurs preferentially from the insertion product of the acrylamide polar monomer.¹⁵ Even for a copolymer with a low DMAA incorporation formed at 20 bar ethylene (entry 1-4) the amide-derived end groups were observable (ethylene- vs amide-derived 1:12). With regard to the regiochemistry of the insertion, both DMAA- and AcAMEA-derived unsaturated end groups observed originate from a 2,1-insertion product exclusively.

The ethylene–AcAMEA copolymer with 6.9 mol % incorporation predominantly possesses acrylate over ethylene-derived end groups both in the saturated and unsaturated end groups (80% acrylate-derived unsaturated end groups, 85% saturated end groups). An analogous pattern of end groups was found previously for ethylene–MA copolymers.^{9e} This suggests that the pendant amide moiety of AcAMEA has no strong influence on the microstructure of the copolymers, as expected. In summary, β -hydride elimination after an acrylamide insertion occurs less readily than in the case of acrylates, which is distinctively reflected in the end group pattern.

Inhibition of Polymerization by Amides. The limited polymerization activities of 1-DMSO in the presence of amide-containing monomer raise the question of the nature of interactions with the metal centers. When a small excess (3–5

equiv) of a nonpolymerizable saturated amide, *N*-methyl acetamide (MAcA) or *N,N*-dimethyl acetamide (DMAcA), respectively, was added to an NMR tube charged with 1-DMSO in methylene chloride-*d*₂ at room temperature, fast exchange of coordinated DMSO and amide was observed. The corresponding highfield-shifted proton resonance of DMSO (δ = 2.65 and 2.70 ppm, respectively) did not correspond to bound (δ = 2.91 ppm) or free (δ = 2.54 ppm) DMSO (Figures S8 and S9, Supporting Information). No further reaction with the acetamides was observed, even after warming the samples to 60 °C for 90 min. This stability of the catalyst precursor in the presence of amides at elevated temperature is in agreement with ethylene homopolymerization data in the presence of DMAcA (Table S1, Supporting Information). Average activities determined from the polymer yields in 15 and 60 min polymerization experiments are similar; in detail, the activity is lower by one-fifth in the one hour experiment. A similar decrease in activity over time was also found in homopolymerizations of ethylene in the absence of any polar additives.^{6g} Catalyst activities in ethylene homopolymerizations employing 1-DMSO decreased with increasing acetamide concentration in the polymerization mixture (Table 2). Compared with a

Table 2. Homopolymerizations of Ethylene in the Presence of Polar Additives^a

entry	additive	additive conc. [mol L ⁻¹]	polymer yield [g]	average TOF ^b [10 ³ h ⁻¹]	M_n^c [10 ³ g mol ⁻¹]	M_w/M_n^c
2-1			4.357	124.3	17.0	2.0
2-2	MAcA	0.002	3.683	105.0	17.0	1.9
2-3	MAcA	0.05	0.366	10.4	10.8	2.1
2-4	MAcA	0.10	0.169	4.8	9.8	2.0
2-5	MAcA	0.20	0.088	2.5	10.7	1.8
2-6	DMAcA	0.004	2.326	66.3	18.2	1.9
2-7	DMAcA	0.05	0.442	12.6	9.7	2.4
2-8	DMAcA	0.10	0.238	6.8	15.6	1.8
2-9	DMAcA	0.20	0.141	4.0	6.7	2.2
2-10	EA	0.05	3.308	94.3	12.1	2.1
2-11	EA	0.10	1.722	49.2	n.d.	n.d.
2-12	DMSO	0.05	0.062	1.8	1.1	1.7
2-13	AcN	0.05	0.926	26.4	n.d.	n.d.
2-14	AcN	0.10	0.678	19.4	n.d.	n.d.
2-15	AcN	0.30	0.291	8.3	n.d.	n.d.
2-16	MES	0.05	1.506	43.0	n.d.	n.d.
2-17	MES	0.10	1.354	38.7	n.d.	n.d.
2-18	PrA	0.05	0.376	10.7	n.d.	n.d.
2-19	PrA	0.10	0.310	8.8	n.d.	n.d.

^aReaction conditions: 2.5 μ mol 1-DMSO, 10 bar, 80 °C, 30 min, total volume toluene + additive 50 mL. ^bTOF in mol(PE) mol(catalyst)⁻¹ h⁻¹. ^cFrom GPC at 160 °C in 1,2,4-trichlorobenzene.

polymerization experiment in the absence of additives (entry 2-1), a 50-fold (MAcA, entry 2-5) and 30-fold (DMAcA, entry 2-9) lowered activity were observed with acetamide concentrations of 0.2 M. Note that this concentration corresponds to the minimum comonomer concentration applied for the copolymerizations (Table 1). For all acetamide concentrations, MAcA showed a slightly stronger inhibition than DMAcA. This can be related to a stronger coordination of secondary vs tertiary amide, likely due to the steric bulk of the latter.¹⁶ This difference in coordination strength may likewise contribute to the higher ethylene pressures required for the NIPAM copolymerizations in comparison with DMAA.

In order to relate the inhibition by amides with other relevant functional groups present in vinyl monomers (or in the labile ligand of the catalyst precursors), ethylene homopolymerizations in the presence of 0.05 M and higher concentrations of various saturated polar-substituted compounds were studied (Table 2 and Figure 1). DMSO (entry 2-12) inhibits

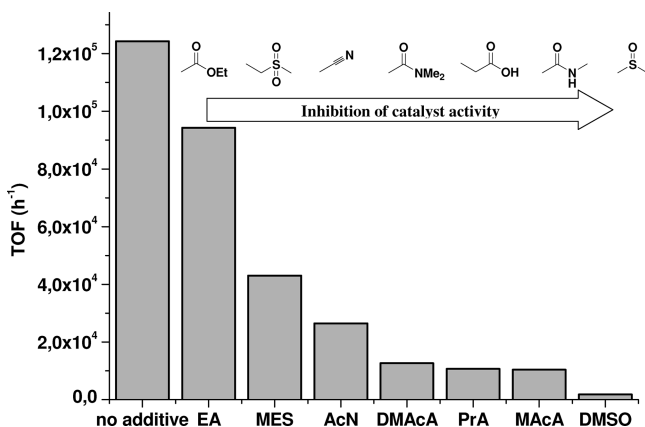


Figure 1. Inhibition of ethylene polymerization by saturated compounds with various polar groups (reaction conditions: 2.5 μ mol 1-DMSO, 10 bar, 80 °C, 30 min, total volume of toluene and polar compound 50 mL, 0.05 M of additive).

polymerization to a slightly larger extent than the amides MAcA and DMAcA, which is in agreement with the aforementioned ¹H NMR study. Ethyl acetate (EA, entries 2-10) exhibits a much lower effect on polymerization by comparison to all other compounds studied. Thus, the much higher polymerization rates in ethylene–acrylate copolymerization vs copolymerization of unsaturated amides can be traced to an inhibition of polymerization by coordination of the amide groups of the free monomer. The inhibition of ethylene polymerization observed for acetonitrile (AcN), methyl ethyl sulfone (MES), and propionic acid (PrA) is in qualitative agreement with previous studies of the corresponding vinyl monomers.^{6b,f,h,17} In this overall scheme, amides inhibit relatively strongly, similar to the carboxylic acid and stronger than the nitrile and the sulfone. For the oxygen-containing monomers, the impact on polymerization can be rationalized by the electronegativity of the oxygen-bound fragments O=X and corresponding expected κ -O-binding strength to the electrophilic metal center (with the exception of the carboxylic acid, which does not follow this trend, possibly because of coordination in its deprotonated form).

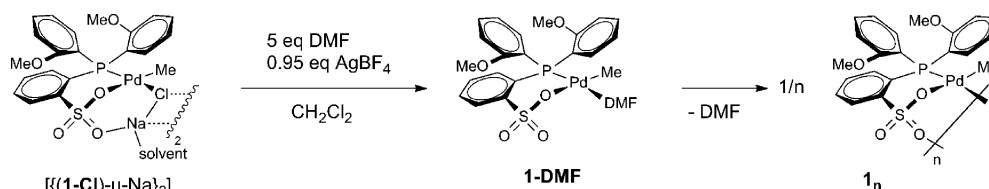
Compared to ethylene homopolymerization in the presence of the saturated amide DMAcA (Table S2, Figure S10, Supporting Information), in copolymerization of DMAA (entries 1-5 to 1-7), activities are ca. 5-fold lowered. This suggests that also coordination of functional groups of

incorporated monomer (vide infra) and slower insertion into electron-withdrawing substituted Pd–alkyls formed after an insertion of polar comonomer by comparison to the unsubstituted alkyls from ethylene insertion affect copolymerization rates, as observed previously for other monomers.¹⁰

The binding strength of the ligand on the fourth coordination site of the phosphinesulfonato Pd(II) methyl catalyst precursor is decisive for its properties in (co)-polymerization reactions. To this end, the relative binding of DMSO vs polar additives was investigated by ¹H NMR spectroscopy. The equilibrium (**1**-DMSO + L $\rightleftharpoons$ **1**-L + DMSO) is fast on the NMR time scale at room temperature; only one DMSO signal (average of **1**-DMSO and free DMSO) is observed upon addition of variable amounts of polar additives to a ca. 40 mM CD₂Cl₂ solution of **1**-DMSO (Supporting Information Figure S11, Table S3). The estimated equilibrium constants $K_{eq}(\text{EA}) < 10^{-2}$, $K_{eq}(\text{MES}) < 10^{-2}$, $K_{eq}(\text{AcN}) \approx 1$, $K_{eq}(\text{DMAcA}) \approx 0.4$, $K_{eq}(\text{PrA}) < 0.1$, $K_{eq}(\text{MAcA}) \approx 0.6$ are in qualitative agreement with the results of ethylene homopolymerization in the presence of 0.05 mol L⁻¹ of the same additive (Figure 1).¹⁸

A more labile coordination in the catalyst precursor allows for copolymerizations at lower ethylene pressures, and therefore higher incorporations of polar comonomer can be achieved. Motivated by the lower inhibition of ethylene polymerization by MAcA and DMAcA versus DMSO, we investigated the formation of a DMF-coordinated [(P[^]O)Pd(Me)] complex (Scheme 2). A procedure similar to the synthesis of **1**-DMSO starting from **1**-TMEDA^{9e} (TMEDA = *N,N,N',N'*-tetramethyl ethylene diamine), that is, repeated evaporation with excess sulfoxide or amide, respectively, to remove the diamine, was studied. This approach resulted in mixtures of starting material and product (**1**-DMF) that could not be separated by means of extraction or crystallization. The mixture was soluble in methylene chloride, and two Pd–Me resonances could be observed at room temperature. The ¹³C carbonyl resonance of DMF was only slightly low-field-shifted to 165.35 ppm (162.49 ppm for free DMF under identical conditions), which indicates a rather weak coordination of DMF. A suitable alternative route is therefore the generation of fragment **1** in the absence of other coordinating reagents than DMF. To this end, chloride abstraction from the recently reported dimeric cation bridged anionic complex [(**1**-Cl)- μ -Na]₂ with silver salts was utilized.^{6g} Stirring of [(**1**-Cl)- μ -Na]₂ with 5 equiv of DMF and 0.95 equiv of silver tetrafluoroborate in methylene chloride for one hour in a sealed tube yielded **1**-DMF as an off-white powder after filtration, removal of the solvent, and washing with diethyl ether. The proton resonances of the coordinated DMF were low-field-shifted compared to free DMF (3.00 and 2.91 ppm for Me protons and 8.13 ppm for the carbonyl bound proton; Figure S12, Supporting Information). However, **1**-DMF is not stable in methylene chloride in the absence of excess DMF and

Scheme 2. Synthesis and Decomposition of 1-DMF



Scheme 3. Synthesis of Dimethyl Acrylamide Insertion Products 3,4

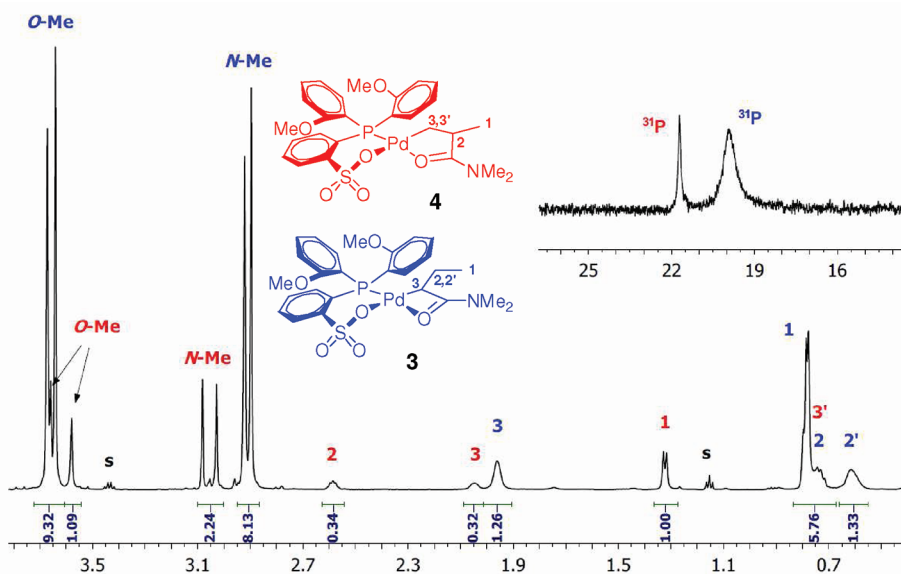
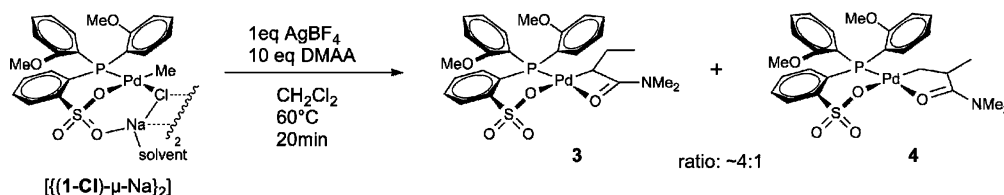


Figure 4. Aliphatic region of ^1H NMR spectra of dimethyl acrylamide insertion products 3,4 (formed in a 4:1 ratio) in CD_2Cl_2 at 25°C . S: Residual Et_2O resonances. Inset: Close up of ^{31}P NMR spectra of 3,4 under identical conditions.

(Figure 4). The ethyl CH_3 protons of 3 appear as a triplet at 0.78 ppm, whereas the methyl protons of 4 show a doublet splitting at 1.32 ppm. Remarkably, the resonances of the diastereotopic methylene protons 3 and 3' in 4 differ by more than 1 ppm. The ^{13}C carbonyl resonances are significantly low-field-shifted to 184.58 ppm for the 2,1-insertion product 3 and 187.30 ppm for the 1,2-insertion product 4, indicating a chelate structure of the complexes, in which the amide group coordinates to the fourth coordination site of the palladium center.²⁰ Also, the wavenumber of the carbonyl stretching band of 3,4 is decreased from 1634 cm^{-1} in free DMAcA to 1584 and 1573 cm^{-1} in the insertion products (Figure S21, Supporting Information). According to the Cambridge Structure Database, $\kappa\text{-O}$ -coordination has been observed exclusively in $\text{Pd}(\text{II})$ amide complexes.²¹ Thus, a similar $\kappa\text{-O}$ -coordination appears likely in 3,4. Noteworthy, the same low-field-shifted carbonyl resonances indicating chelate formation were observed in the (contaminated) insertion products starting from 1-DMSO. In contrast, single insertion of MA results in the formation of the 2,1-insertion product $[(\text{P}^{\text{O}})\text{Pd}\{\text{CH}(\text{CH}_2\text{CH}_3)\text{C}(\text{O})\text{OMe}\}\text{-(DMSO)}]$ exclusively, in which DMSO coordinates to the Pd center rather than the chelating coordination of the ester moiety in the alkyl fragment. This different behavior relates to the above conclusions on coordination strength of amide moieties, as derived from the extent of inhibition of polymerization (Figure 1).

Reactivity of Dimethyl Acrylamide Insertion Products.

Further chain growth requires π -coordination of olefinic monomer to the Pd center and hence opening of the $\kappa\text{-O}$ -coordinated chelate in 3,4. To this end, the coordination

behavior of the monomers and other relevant ligands to the presumed catalyst resting state was investigated. Note that an opening of a chelate by coordination of an incoming ligand will be favored at low temperature because of the unfavorable entropic contribution.

Coordination of ethylene (10 equiv in solution) to 3,4 was not observed even at -80°C by ^1H NMR. However, 3,4 are precursors to highly active ethylene polymerization catalysts even at a low ethylene pressure of 2.5 bar (Table 4). Activation

Table 4. Ethylene Homopolymerizations with 3,4 as a Catalyst Precursor^a

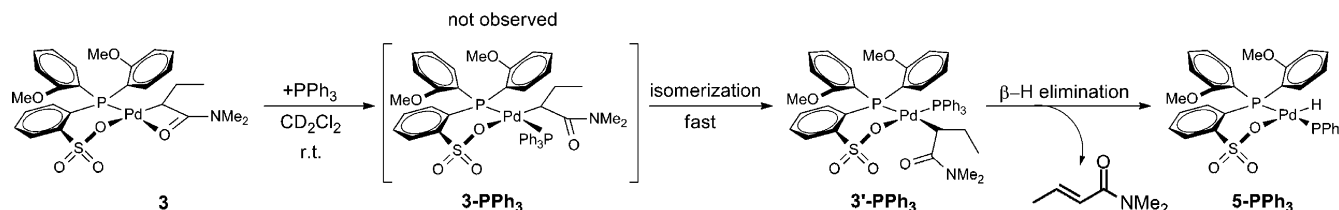
entry	p [bar]	polymer yield [g]	average TOF ^b [10^4 h^{-1}]
1	2.5	1.63	4.7
2	5.0	3.19	9.1
3	7.5	4.07	11.6

^aReaction conditions: $2.5\text{ }\mu\text{mol}$ 3,4, 30 min, 80°C , 50 mL of toluene.

^bTOF in $\text{mol}(\text{ethylene})\text{ mol}(\text{catalyst})^{-1}\text{ h}^{-1}$.

for polymerization requires coordination and insertion of ethylene, but after a few insertions have occurred, the active species will no longer be prone to chelating coordination of the amide end group because of an entropic disfavoring of large ring chelates. Thus, even if chelate opening by ethylene binding to 3,4 is unfavorable, the latter can be converted to the active species eventually. Polymerization activities are little dependent on ethylene concentration at pressures above 5 atm. Accordingly, at 10 atm, activities are similar to polymerizations with the labile-coordinated 1-DMSO as a catalyst precursor.

Scheme 4. Reactivity of 3,4 toward Triphenylphosphine



No coordination of DMAA or DMSO, respectively, was observed in the presence of up to 20 equiv at room temperature (Figures S22-1 to -3, Supporting Information). Both ^{13}C carbonyl resonances of **3,4** remained unaltered. However, small amounts of *N,N*-dimethylcrotonamide (DMCA), formed by β -H elimination from the 2,1-insertion products, were found after 24 h. By comparison, **3,4** is virtually stable over this period of time in methylene chloride solution in the absence of additional reagents. The four-membered chelate of **3** was readily opened in the presence of equimolar amounts of PPh_3 and undergoes rapid β -H elimination (Scheme 4). The two ^{31}P resonances of the opened chelate **3'-PPh₃** show a doublet splitting with $^2J_{\text{PP},\text{cis}} = 39$ Hz. No opened chelate with a trans coordination of the phosphorus atoms (**3-PPh₃**) was observed, assumingly because of the trans-effect of the phosphines. The organic product of β -H elimination (DMCA) as well as the resulting metal hydride complex (**5-PPh₃**) appear in ^1H and ^{31}P NMR spectra (Figures S23 and S24, Supporting Information). By contrast, the five-membered chelate **4** was stable under these conditions even with an excess of PPh_3 .

The weaker σ -donor pyridine coordinates to **3** in an observable equilibrium at room temperature, whereas **4** retained its chelated structure as expected from the aforementioned studies. About 2 equiv of pyridine were required to completely form the opened chelate **3-PYR**. **3-PYR** is relatively stable toward β -H elimination in the presence of excess pyridine. After 24 h, only trace amounts of **5-PYR** and DMCA were observed along with the isomerized complex **3'-PYR** (for numbering cf. Scheme 4). By comparison to pyridine, 2,6-lutidine is believed to possess a weaker coordination strength due to steric hindrance. Both opened chelate **3-LUT** and **3** can be observed simultaneously in the presence of 2 equiv of 2,6-lutidine at temperatures between 273 and 298 K. On the basis of the ratio of **3** and **3-LUT** obtained from ^{31}P NMR peak areas, the equilibrium constants $K(T) = [\text{3-LUT}]/([\text{3}] + [\text{2,6-lutidine}])$ were calculated. Values for the reaction enthalpy $\Delta H^\circ = -41.8(10.5)$ kJ mol $^{-1}$ and entropy $\Delta S^\circ = -115(37)$ J mol $^{-1}$ K $^{-1}$ were obtained by a Van't Hoff plot (Figure S25, Supporting Information). Such a negative enthalpy and unfavorable entropy are generally expected for chelate opening reactions, and the values found are in the same range as reported for similar chelate opening reactions with ester-derived five- and six-membered chelates in cationic α -diimine complexes.^{3b,22,23} Extrapolation of the thermodynamic data to typical polymerization conditions with $[\text{2,6-lutidine}] = 1$ mol L $^{-1}$ yields $K(358\text{ K}) \approx 1.5$. Considering the higher coordination strength of 2,6-lutidine in comparison to DMAA and ethylene (with typical concentrations of both monomers being on the order of a mol L $^{-1}$ in polymerizations), it can be concluded that chelate species formed after an amide insertion will be relevant species in copolymerizations and retard polymerization.

SUMMARY AND CONCLUSIONS

These combined comprehensive experimental studies of polymerization and stoichiometric insertion reactions reveal fundamental features of insertion polymerization of amides. Other than the somewhat electron-poorer carbonyl group of acrylates, free amides coordinate strongly to the catalyst studied, and hereby the polar monomer itself reversibly retards polymerization. However, the catalysts are stable in the presence of amides, and no indication of irreversible deactivation pathways specific to amide monomers was observed. Chelating coordination of amide moieties of polar monomer incorporated in the growing chain also contributes significantly to lower rates of copolymerization vs ethylene homopolymerization. In detail, these chelates appear to be more stable than corresponding ester chelates, and the impact on polymerization rates is slightly more pronounced than for acrylate copolymerizations. Insertion occurs preferentially in a 2,1-fashion, as expected for electron-poor vinyl monomers because of the strong prevalence of electronic factors in the absence of specific bulky substitution patterns of the catalyst.^{9f} 1,2-Insertion is also clearly observed (ca. 20%) and occurs to a larger extent than found for acrylates.^{9e,10} This is in-line with electronics determining the regioselectivity, which will be higher for the electron-poorer olefin. Net insertion rates into a Pd-Me bond of the secondary and tertiary amides studied are ca. 4- to 8-fold lower by comparison to methyl acrylate. Note that these data include the coordination preequilibrium of displacement of DMSO and competitive κ -O amide binding vs the required π -coordination of the vinyl group. Though consecutive insertions of amide monomer in copolymerizations are unlikely because of their limited incorporation, stoichiometric studies reveal that consecutive insertions of the secondary amide *N*-isopropylacrylamide can occur. Chain transfer occurs more rapidly from the insertion product of the polar amide monomer, Pd-CH(CONR $_2$)-CH $_2$ -R, by comparison to the unsubstituted alkyls from ethylene chain growth, as is evident from end groups observed in the polymers studied in this work and is also supported by observation of β -hydride elimination in stoichiometric studies.

Overall, the copolymerization is limited most decisively by the combination of retardation of polymerization by reversible blocking of the coordination site by the amide groups of free monomer and a limited insertion rate. This results in an intrinsic trade-off between the amide content of the copolymer and copolymerization productivity. Other than retardation of polymerization by formation of chelates by polar moieties incorporated in the growing polymer chain, this can not be counterbalanced by increasing the monomer concentrations. In a general view of Pd(II)-catalyzed copolymerization of polar vinyl monomers CH $_2$ =CHX, this comprehensive experimental study of amide copolymerization, together with the inhibition studies reported and a recent detailed theoretical study of acrylonitrile copolymerization¹⁷ and mechanistic study of

acrylate polymerization,¹⁰ evolves the criteria for a privileged monomer. While a retardation of polymerization by slower insertion into the α -X substituted alkyl formed by incorporation of polar monomer as well as by chelating κ -X coordination of comonomer-derived repeat units appear to be general phenomena of such copolymerizations, the weak coordination of the ester group of acrylate monomer ultimately is responsible for the accessibility of ethylene copolymers with high incorporations of the polar comonomer.

In the context of these considerations, it is notable that to date no specific irreversible deactivation reactions of neutral Pd(II) polymerization catalysts have been reported for any polar vinyl comonomer, although they likely occur in some cases.

The aforementioned limitations being understood, they should not obscure the fact that this insertion copolymerization provides a useful access to amide-substituted polyethylenes, which is not sensitive to the nature of the amide substitution pattern.

■ ASSOCIATED CONTENT

■ Supporting Information

Supplemental tables and figures, general experimental procedures, synthesis, additional NMR spectra, polymerization data, and crystal structure of **2-MeOD**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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